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ORIGINAL CONTAINS
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**The Growth of Zinc Selenide Single Crystals
by Physical Vapor Transport in Microgravity**

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Crystal Growth Studies

A schematic diagram of the three-zone translational furnace reported previously is shown in Figure 1 and the tube cross-section is shown in Figure 2. Isothermal furnace liners (heat pipes) are used to produce uniform temperatures in the source zones and the growth zones, respectively. Figure 3 shows the temperature control system. The center zone is controlled by a Barber-Coleman model 570 programmable temperature controller. It also controls the setpoints of two Barber-Coleman model 560 controllers for the right and left zones through the remote setpoint output. A few thermal profiles of the furnace are shown in Figures 4&5. Note that small discrepancies exist between the setpoint temperatures and the actual zone temperatures. Such differences are due simply to the position of the setpoint thermocouple and are immaterial.

In order to maintain the growth interface at the same position in the thermal profile, one must move either the ampoule or the furnace. In our earlier work ¹⁻⁵, we moved the ampoule periodically, but with this system it is possible to move the furnace at rates as low as 1 mm/day. It is anticipated that the greater stability of this system will yield crystals of better quality. A plot of furnace speed versus the dial setting of the motor drive is given in Figure 6.

Five growth runs of 12.5 days each have been made using a translation speed of about 3 mm/day. The heating/cooling program used for the center zone was as follows:

23°C to 500°C in 1.5 hr
500°C to 970°C in 1.5 hr
970°C for 300 hr
970°C to 500°C in 20 hr
Power off and furnace cool

Growth data for the five runs are given in Table I. The highest growth rate obtained thus far is 657 mg/day. The crystals obtained from these five runs are shown in Figure 7. The first crystal is displayed in Figure 8. It was grown in the 951/933 profile of Figure 4. It has smooth faces and appears to be a single grain. It has a cross section of about 50 sq mm and is about 1 cm long. Crystal number 4 is depicted again in Figure 9. It was grown in the same thermal profile as number 1. Crystal number 5, which was grown in the 967/916 profile (Figure 5) is shown in Figure 10. This crystal had the largest growth rate, which is what one would expect from the large temperature difference, and it is multi-grained. Its uncharacteristic brown color is due to oxidation which occurred when the ampoule cracked. Thin wafers have been cut from some of these crystals and work is now underway on determining dislocation densities and the extent that twinning has occurred.

During the next six months, work will continue on growth studies and characterization of the crystals. Also, an effort has begun on determining the transport rates in the case of vertical transport where convection should have a larger effect

Mass Spectroscopy Studies

1. Task Description

This task includes studies of:

- a) The high-temperature outgassing behavior of the silica ampoule material in order to develop a cleaning and bake-out procedure that will minimize the amount of impurities introduced into the vapor from the ampoule materials and in particular during the seal-off procedure.

b) The outgassing behavior of the ZnSe starting material during high vacuum refinement at elevated temperatures in order to develop a temperature-pressure program that will optimize the removal of impurities while minimizing a shift in stoichiometry due to preferred evaporation of the higher fugacity component.

2. Description of system and operation

The mass spectrometer system has been essentially completed and, after calibration, will be used to pursue the above tasks. In the following we describe the system and essential operation procedures in some detail.

Effusion furnace:

The furnace assembly consists of three subassemblies: (a) The molybdenum double furnace described in the first semiannual progress report. (b) A furnace housing. (c) The mechanical elevator and its case. Each of these subassemblies had to be modified before the furnace could be assembled.

a) The top furnace lacked a control thermocouple. A W5Re/W16Re thermo-couple (Type C) was brought up the outside of the water-cooled stainless steel furnace shell in an Al_2O_3 double bore 0.125" tube. The alumina tube was fastened to the furnace shell by a stainless steel clamp extending from the case bottom half way up the shell. This was necessary to maintain positional stability of the thermocouple. The alumina tube extends to the top of the shell and thereafter the bare thermocouple wire was bent over the top and down into the furnace. It is essential that no

oxide extend into the furnace because the reflecting heat shield is made of tantalum which will react with any oxide when the metal is hot.

As delivered, the furnace base plate only supported the water tubes in such a way that strain is relieved as the furnace is raised and lowered. Therefore a plate was added to clamp all electrical leads (heater power and thermocouples) as well as water tubing and to provide guidance around the elevator mounting plate. The thermocouple's leads are held in place by a rounded kink on either side of this plate. This additional strain relief plate is separated from the furnace base plate by one inch stainless steel spacers and all connections are made in this space.

b) The furnace case originally consisted of a stainless steel tube with six-inch CF flanges on each end. Its overall length is 22.25". A tube terminated with a four-inch CF flange extends 10" overall from the main tube for connection with a trapped diffusion pump station. A six-inch CF flange mounted as close as possible to the main tube provides access to the tube tangent to the main housing tube 1-7/8" below the upper flange and a 1" ISO-KF flange and tube 4" below the top flange opposite the 6" flange. The 2.75" flange provide a furnace view port and the 1" flange provides Penning gage, calibration substances, and back-filling gas connections through an ISO tee.

c) The furnace elevator case was modified by adding a 2.75" CF flange cover with two 0.25" stainless steel tubes for cooling water connections and a 4.50" CF flange cover with two electrical and thermo-couple feedthroughs. Each feedthrough contains two 15 amp electrical connections and one type C thermocouple connector.

d) Assembly of the effusion furnace proceeded by mounting the strain relief ring on the elevator plate. The cooling water tubing was brought from the 0.25" Swagelock fittings at the furnace plate through 0.25" tubing silver soldered to 0.125" copper tubing wound in a 12-loop spiral with a diameter approximately 0.50" less than the inside diameter of the furnace case. These copper tubes pass through the 0.25" stainless steel tubes of the 2.75" flange on the elevator case. They are sealed with a viton o-ring compression fitting. This design leaves only the fitting at the furnace bottom plate as a possible water leak and the 12-coil spiral is sufficiently flexible that the elevator lock mechanism can hold the elevator at full extension without slipping. An additional advantage is that the torsional rotation of the tubing from full elevator extension to minimum extension is small and this plumbing should have a long trouble free life. The thermocouples and power leads are connected at the furnace base plate to leads coiled inside the water line coils. All connections are made with beryllium-copper gold plated tube clamps. The furnace plate and strain relief plate isolate these clamps from any tension as the furnace is raised and lowered. The thermocouples were connected with 24Ga type C extension wire insulated in loose fitting Teflon tubing perforated at 1.5" intervals. The power leads are 18Ga copper insulated in the same way that the thermocouple leads were. One side of each furnace was wired in common so that only three power leads were required. Each furnace lead and its thermocouple were brought through the 4.50" flange in a separate feedthrough marked top and bottom. The common is marked with a red dot on the feedthrough. These posts are connected on each furnace feedthrough.

Furnace controller

A furnace control and bakeout circuit have been constructed on a 19" rack panel. In the furnace control mode an Omega CN1200 controller senses the furnace temperature through the type C thermocouple and switches the low side of a variable transformer through a solid state relay. The controller has proportional, rate and integral action. This simple system is adequate for effusion studies. The advantage of using a variable transformer is that it prevents furnace run-away in the event of a catastrophic relay or controller failure. The panel contains a voltmeter that allows us to set a maximum temperature from EPI furnace calibrations. The panel is wired so that the output of the variable transformer can be switched to a bakeout mode. The system consists of two such control and bakeout circuits which share a common switchable meter.

Bakeout system

In addition to the two variable transformers in the control panel, two other variable transformers are wall-mounted. Two Thermolyne FG HIG 1" x 8' tapes heat the mass spectrometer and the pump out tube to the turbomolecular pump. These are operated from the control panel. Two FG HIG 1" x 8' tapes heat the furnace housing and the tube connecting the furnace to the liquid N₂ trap. A similar 1" x 6' tape heats the housing of the elevator and is operated in parallel with one of the furnace housing tapes. These are operated from the wall mounted variable transformers.

An Omega DP462 readout with a six thermocouple capacity allows us to

monitor tape temperature during bakeout. The type K thermocouples are placed on the apparatus at positions where critical bakeout temperatures should not be exceeded.

Cold trap control

An automatic liquid nitrogen controller, MDC model LC-11A has been installed to permit unattended operation of the mass spectrometer and effusion furnace.

Calibration system

A system to allow the introduction of known gaseous compounds into the mass spectrometer has been designed and parts ordered. At present it is sufficiently complete to allow mass calibration of the system.

Furnace operation

EPI recommends furnace bakeout at 800C without water cooling, but because of the Teflon insulation this installation should not be heated that hot without water cooling. The furnace has been heated to 200C and the housing to 100C. Without cooling the liquid nitrogen trap the ultimate pressure above the diffusion pump was less than 1×10^{-7} (the limit of the Penning gage). At the furnace gage port the pressure was 4×10^{-7} . With the diffusion pump valve closed a slow increase in pressure was observed to about 7×10^{-6} . The absence of leaks indicates the bakeout temperature was too low or the bakeout too short. The maximum bakeout temperature of the furnace will be determined experimentally by observing the composition of the gases released as the temperature is increased.

All furnace controls function correctly.

Protective systems

The vacuum systems were supplied with adequate power failure protection. The Balzers forepump has three separate automatic valves built-in to prevent oil from entering the diffusion pump and a mechanical switch that must be reset in the event of a power failure. The Pfeiffer turbomolecular pump station has a similar electrical shutoff mechanism and when the turbine slows to a particular speed a valve vents the high pressure side of the turbine to the atmosphere. This latter feature exposes the effusion furnace to the atmosphere. If this occurs while the furnace is at high temperature, it will be destroyed. To protect the furnace this valve will be connected to the inert gas system used to backfill the vacuum system. A reset electrical power circuit has been constructed to prevent all electrical equipment from restarting when power is restored after a power failure.

Mass spectrometer

Apparently the mass spectrometer was misaligned during the move from the upstairs laboratory to D-20. As usual the RF unit was badly out of calibration. Complete retuning to the mass range 0 to 1023amu largely corrected the calibration problem. Optimizing the voltages V0 to V6 and the RF gave a resolution of less than 0.5amu for strong spectral peaks as recorded on a HP 7034A XY recorder. The QMG-511 is functioning satisfactorily. With a bakeout of only 150C, the base pressure of the isolated mass spectrometer was 5×10^{-9} .

Teknivent's Vector One mass spectroscopy program has been installed on a Mitac AT clone computer and interfaced to the Balzer's QMG-511. Full computer control of the mass spectrometer has been obtained.

Items to be considered and work needed for full completion of mass spectrometer facility

Several literature items are missing. The calibration certificate supplied with each mass spectrometer cannot be located. Balzers cannot supply a copy. We will make one for the current state of the machine. The circuit diagram book is missing. We should purchase one from Balzers while they are still available for this model.

The only construction remaining to be completed is the gas calibration and filling system. Some known samples with high mass fragments must be obtained to complete the calibration.

Modelling of Physical Vapor Transport Rates

Under this task we are developing a numerical model for the transport rates to be expected for ZnSe under given sets of thermal and geometrical boundary conditions, in order to provide guidance for an advantageous conduct of the growth experiments.

As described in detail in the first semiannual report, comparison of our numerical results obtained with the commercial code PHOENICS (CHAM International) with our definitive transport data obtained earlier revealed some serious errors in the code when used in cylindrical coordinates. In response to our detailed documentation, CHAM London acknowledged the error in the program and sent a coding supplement which

supposedly corrected the errors. After detailed testing and comparison of the results for a cylindrical benchmark problem, we found that the supplement, though better than the original code, was still unacceptable. Professor Spalding, the CEO of CHAM, during a recent visit to our Center, promised help and provided a copy of a new, yet unreleased version of the code (PHOENICS 1.5) which we then tested on the VAX 11/785 and the IBM mainframe of CHAM Huntsville. Unfortunately, the error still persists in PHOENICS 1.5!! However, as of one week ago, we have received a new version of the code FIDAP (Fluid Dynamics International) that now allows the description of 2-component flows. The earlier version of FIDAP, with which we have five years of very favorable experience, was limited to monocOMPONENT fluids. We are in the process of adapting this code to the physical vapor transport model.

Once the benchmarking of our numerical model for the iodine/C₄F₈ is completed, we will have established confidence in our PVT model. For its application to the vapor transport of ZnSe in the continuation period, we do not expect any major problems.

References

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4. Elmer E. Anderson, Hai-Yuin Cheng, and Michael J. Edgell, *Mat. Res. Soc. Symp. Proc.* 152, 51 (1989).
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| Run No. | Material Transported (grams) | Average Growth Rate (mg/day) |
|---------|------------------------------------|------------------------------------|
| 1 | 1.9 | 152 |
| 2 | 6.27 | 502 |
| 3 | 0.755 | 60 |
| 4 | 2.90 | 232 |
| 5 | 8.21 | 657 |

Table I. Growth runs

Three Zone Furnace

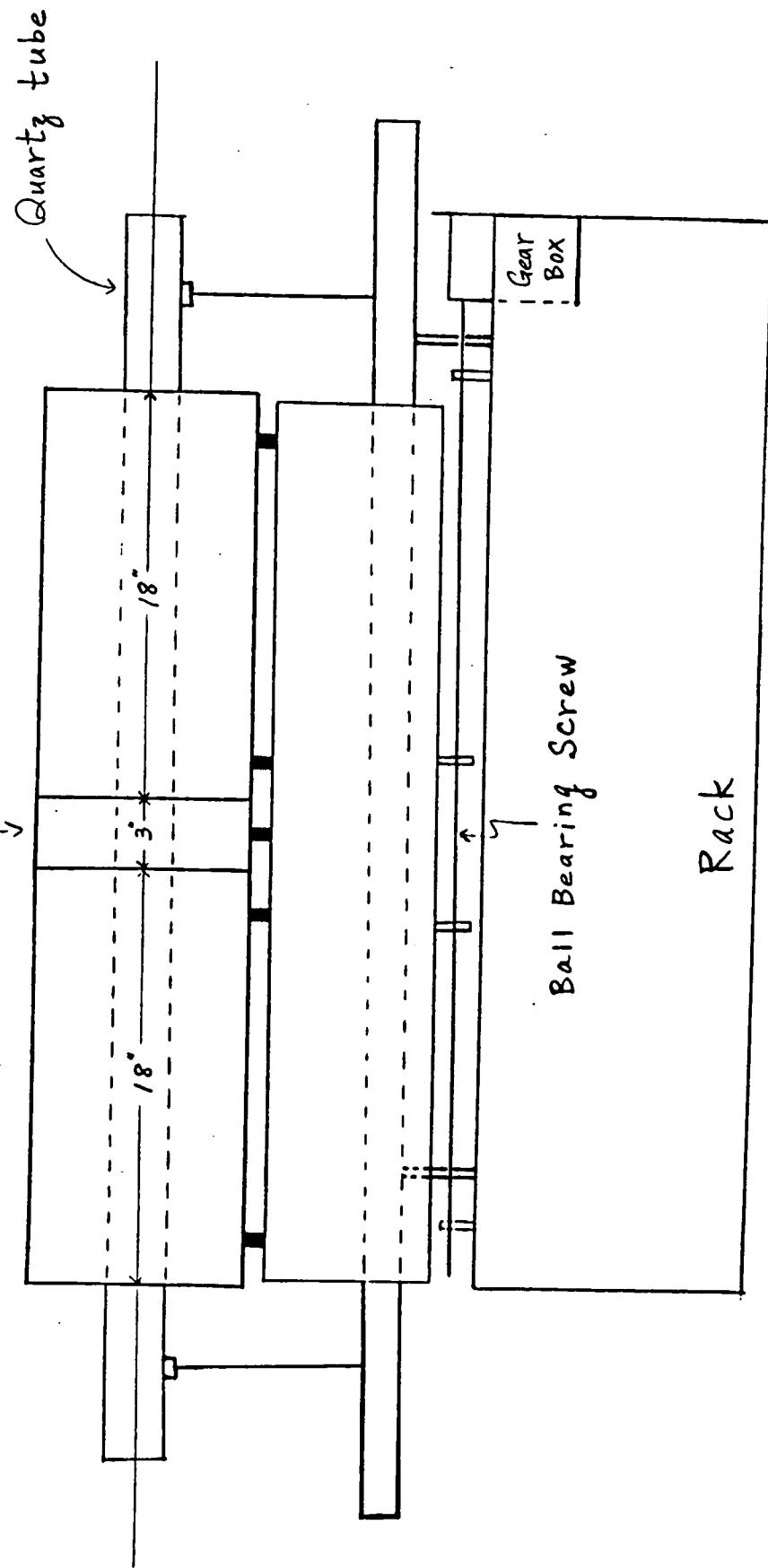


Figure 1. Translational system

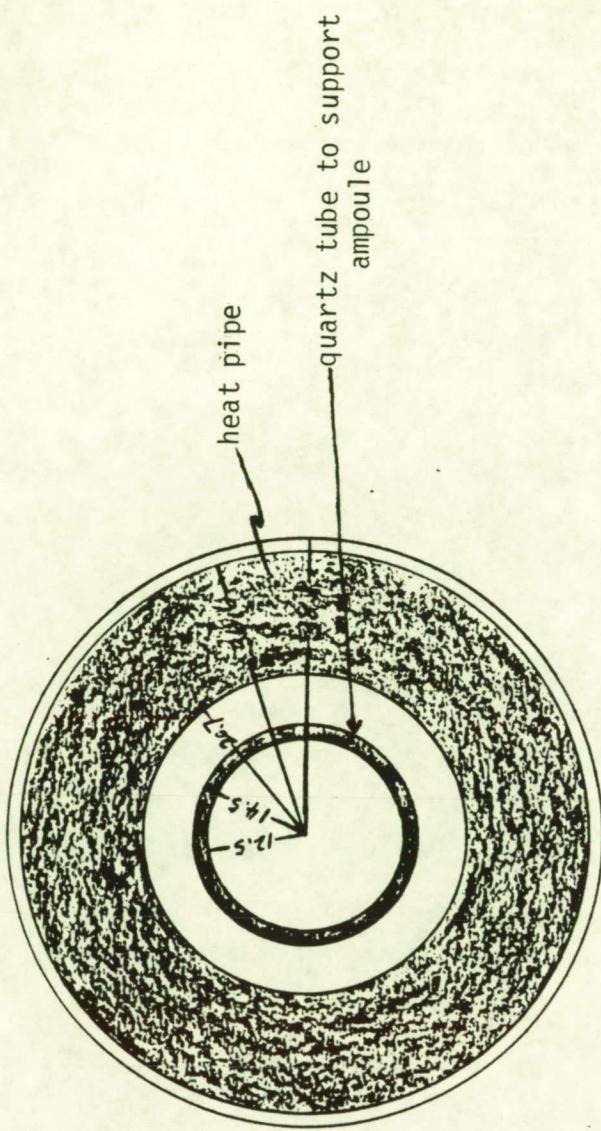


Figure 2. Cross section of furnace tube

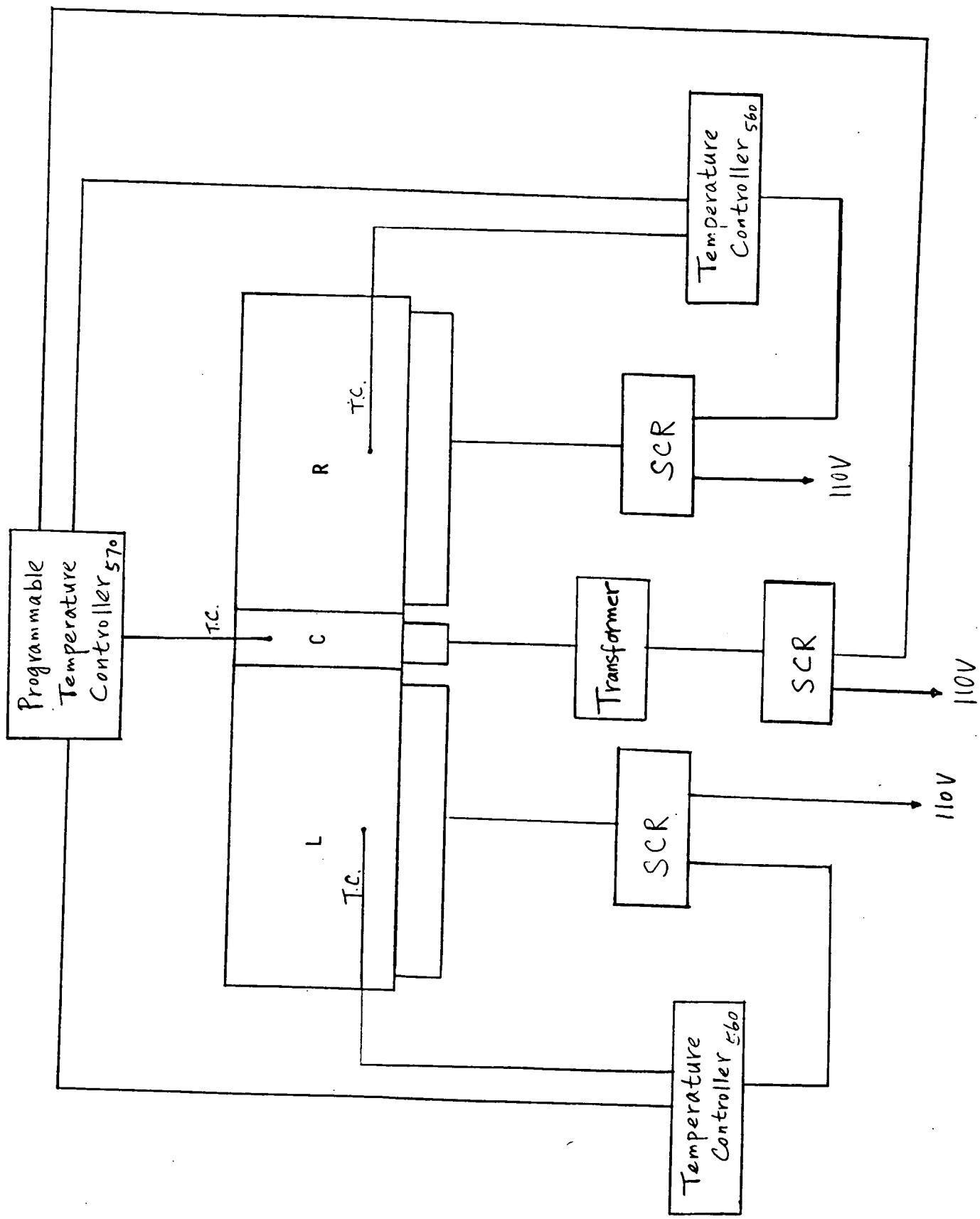


Figure 3. Temperature control system

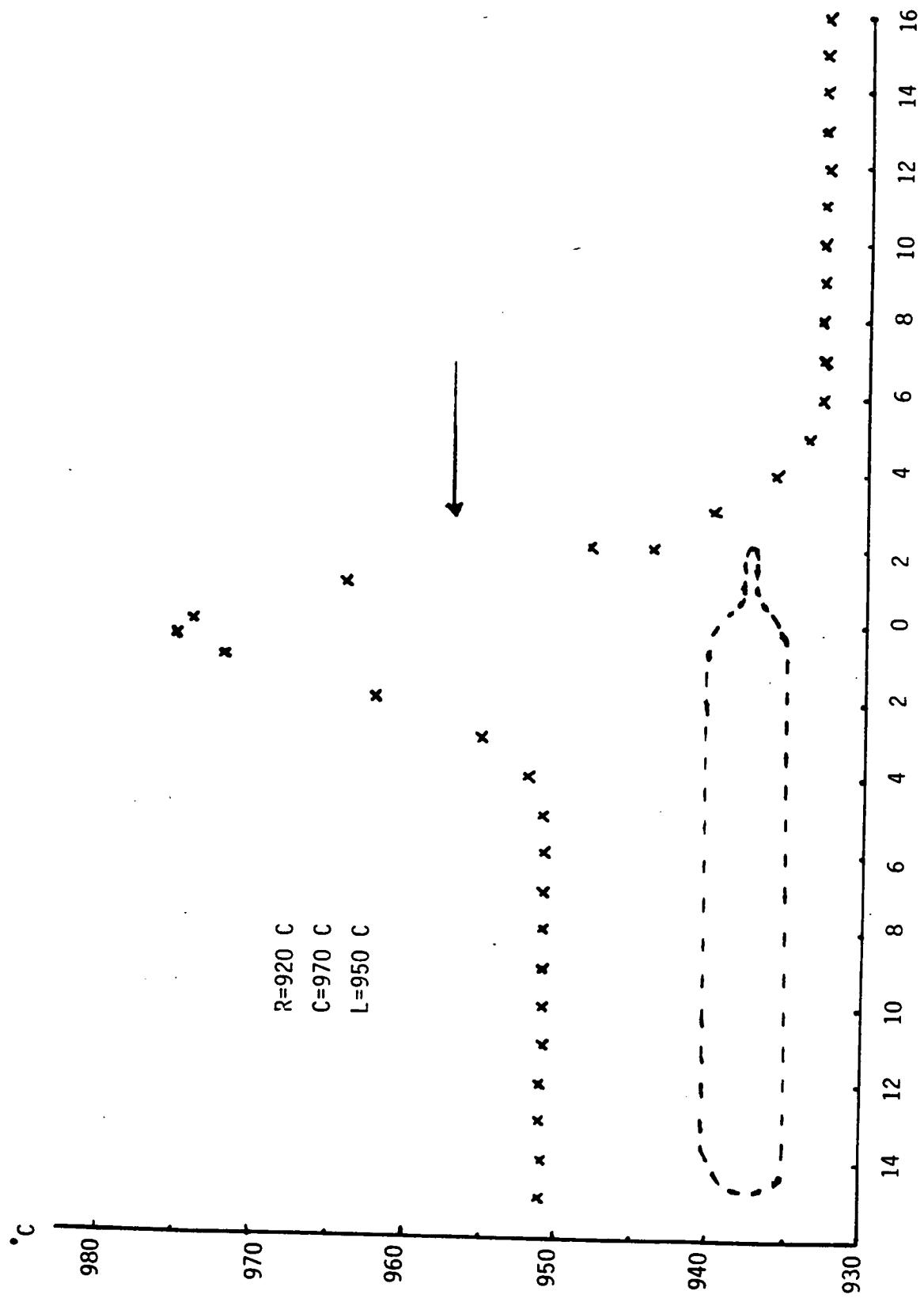


Figure 4. Temperature profile for runs 1 & 4

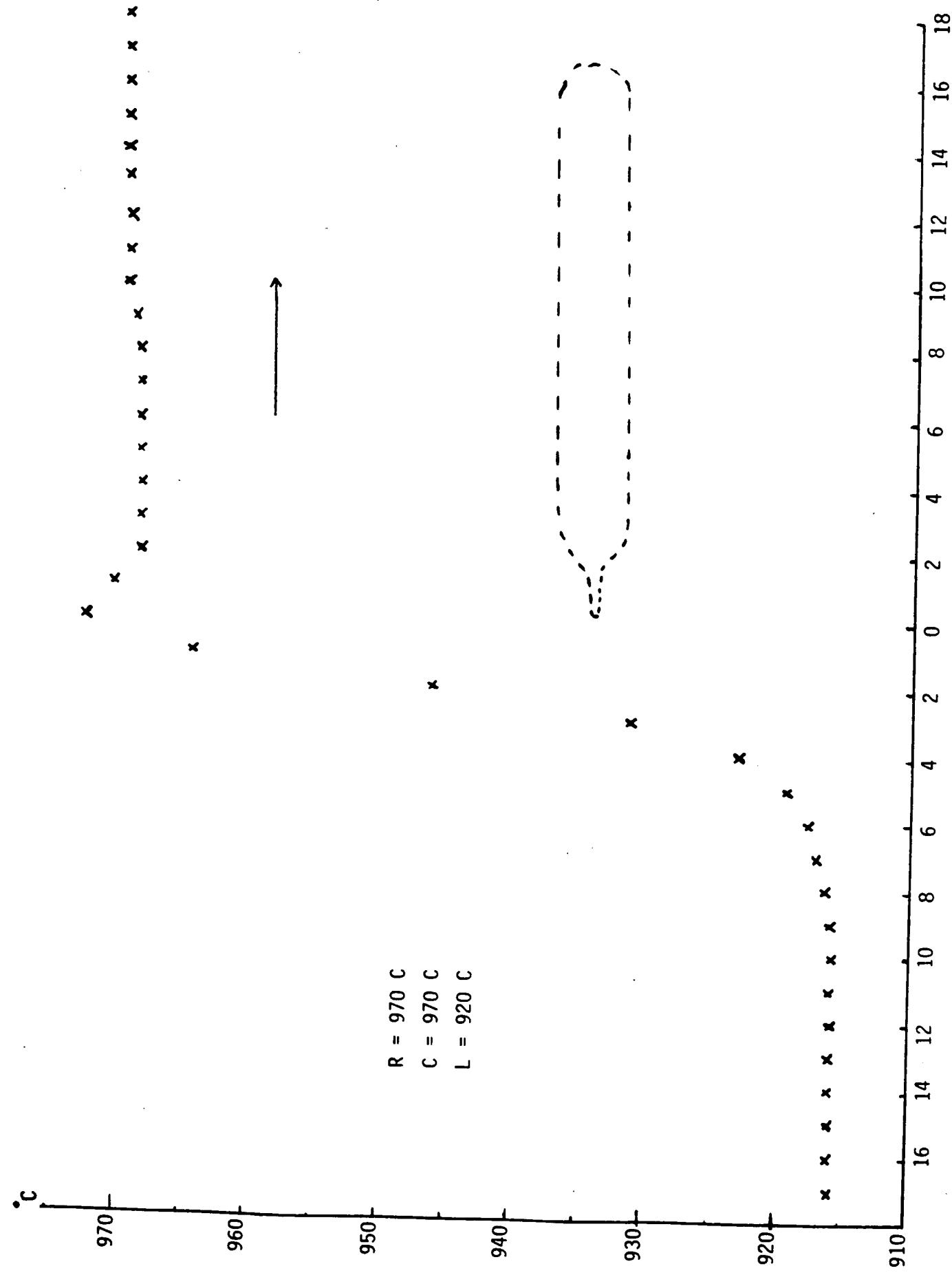


Figure 5. Temperature profile for run 5

Travelling Furnace Speed

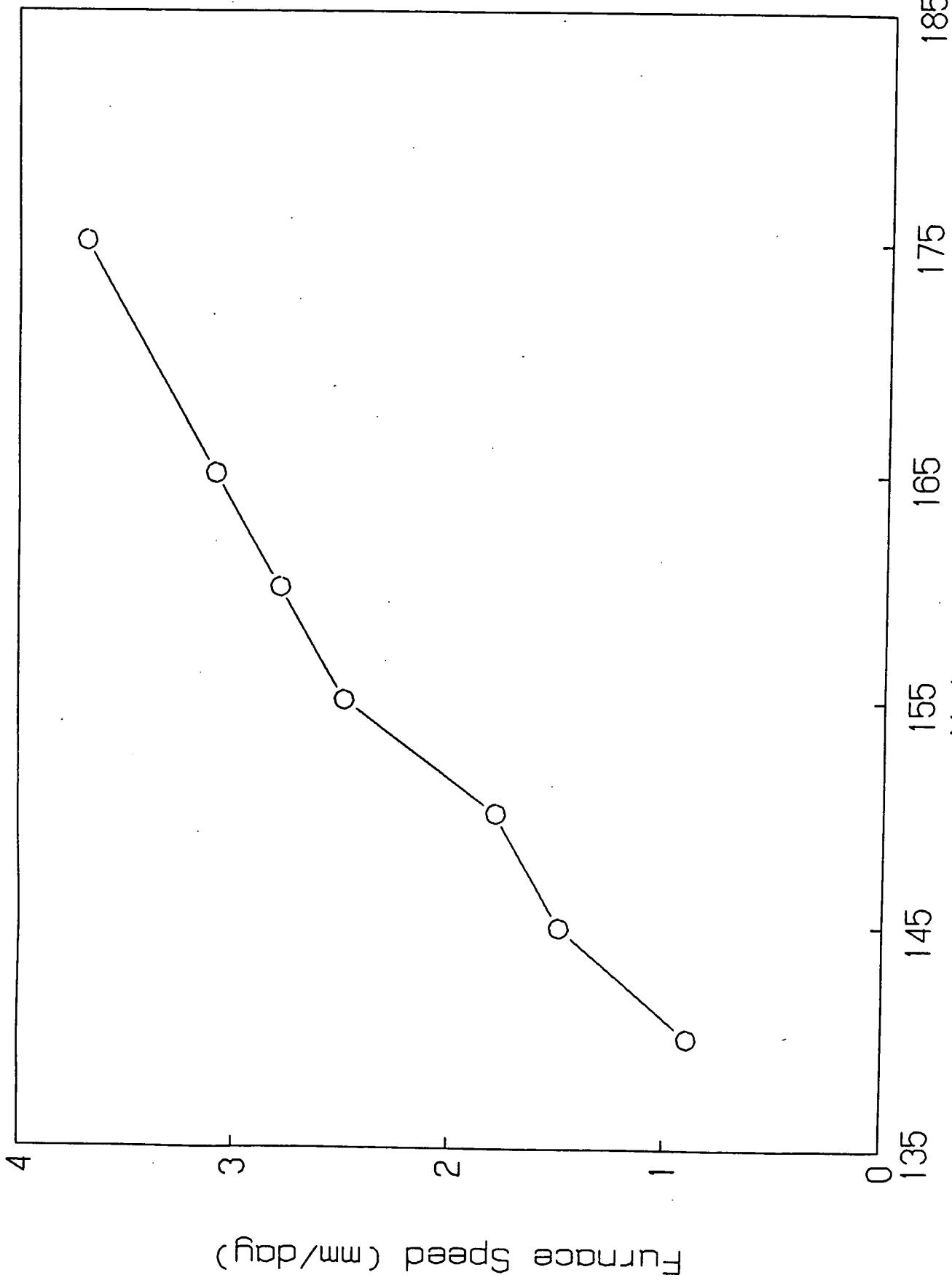


Figure 6. Furnace speed versus dial setting

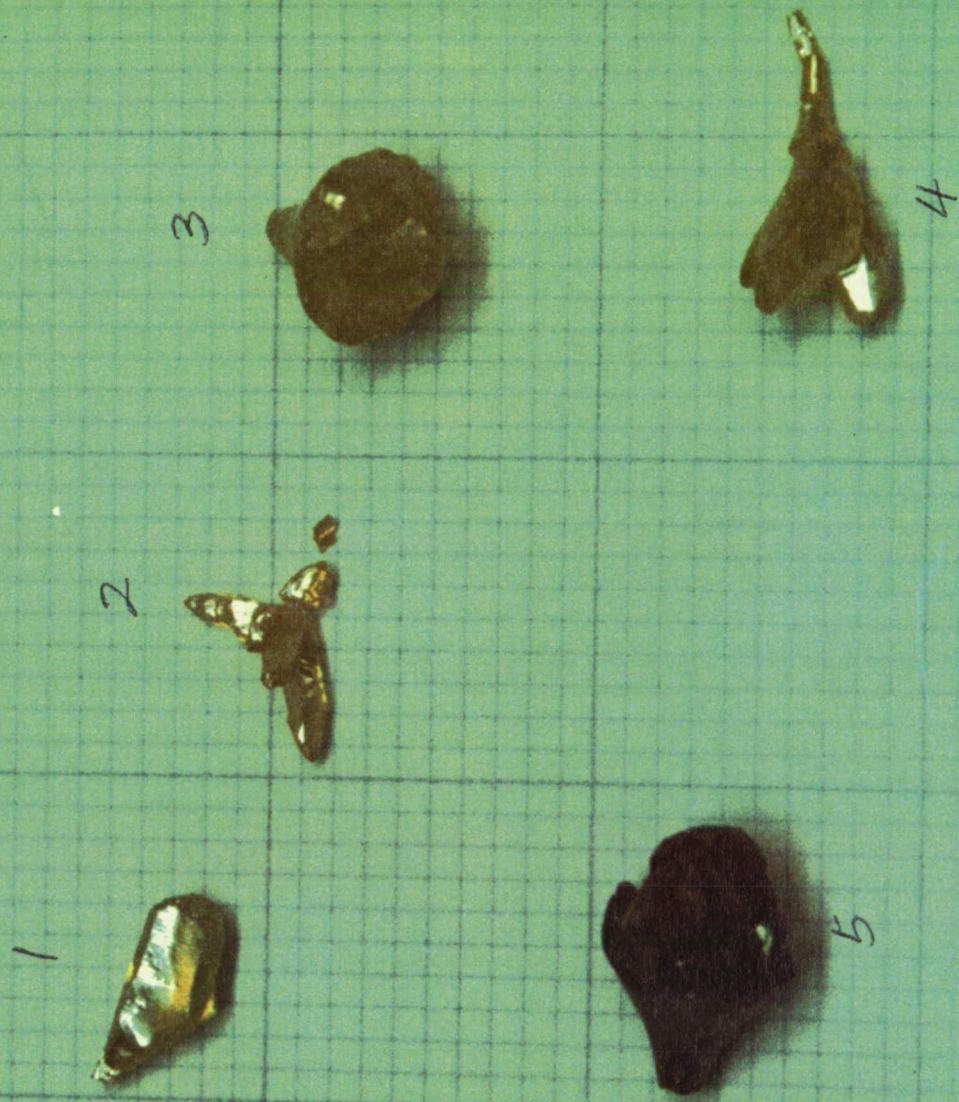


Figure 7. Crystals obtained from the runs in Table I.
The scale is in units of 0.1 inch.



Figure 8. Crystal #1 grown in the thermal profile of Figure 4.
The scale is in units of 0.1 inch.



Figure 9. Crystal #4 grown in the thermal profile of Figure 4.
The scale is in units of 0.1 inch.

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Figure 10. Crystal #5 grown in the thermal profile of Figure 5.
The scale is in units of 0.1 inch.

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